cient magnitude to indicate a possible tendency toward an electronic shift in the neighborhood of the bond.

The alcohols, ethers, aldehydes and ketones have moments of the same order of magnitude as that of water, as required by the hypotheses as to their molecular structures, while ammonia and the amines have smaller moments than water, the difference being somewhat greater than that predicted on the basis of molecular structure alone, because of the fact that the electrons around the nitrogen nucleus are more easily displaced than those around the oxygen nucleus.

The mutual repulsion of the groups attached to the oxygen in the alcohols and ethers, the carbonyl carbon in the aldehydes and ketones, and the nitrogen in the amines, tends to decrease the moment of the molecule, the effect depending upon the resistance of the binding electron pairs to displacement from approximately symmetrical positions.

Among the hydrogen and the organic halides, the moments of the iodine compounds are lower than those of the analogous bromine compounds which, in turn, are lower than those of the analogous chlorine compounds, the inverse of the relative ease of electronic displacement in the halogens. In these compounds, the mutual repulsion of two halogen atoms decreases the moment of the molecule, the accompanying shift of the pairs of binding electrons adding to the decrease.

In the substances discussed the principal doublet in a molecule induces secondary doublets, which act in the same direction as the principal doublet, so that the moment of the whole tends to increase with increasing size of the molecule.

PRINCETON, NEW JERSEY

---

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 46]

# THE AMMONIA, CARBON, HYDROGEN CYANIDE, HYDROGEN EQUILIBRIUM AND THE FREE ENERGY OF HYDROGEN CYANIDE

BY RICHARD M. BADGER

RECEIVED MAY 28, 1924 PUBLISHED OCTOBER 4, 1924

## Introduction

Probably the first synthesis of hydrogencyanide was effected by Clouet[1] by passing ammonia over wood charcoal at red heat. The reaction involved in this experiment is: $NH_3 + C(s) = HCN + H_2$. This reaction has subsequently been quantitatively studied, and its use has frequently been proposed for the commercial synthesis of hydrogen cyanide. Thus Bergmann[2] found that even at 1100° the reaction was measurably slow,

---

[1] Clouet, *Ann. chim.*, **11**, 30 (1791).

[2] Bergmann, *J. Gasbel.*, **39**, 117 (1896); see *Chem. Zentr.*, **49**, 943 (1896).

but that a considerable proportion of ammonia decomposed into nitrogen and hydrogen. The yield of hydrogen cyanide increased with temperature, and at 1300° the greater part of the ammonia was converted into cyanide. Lance[3] obtained even larger yields, and found that when the gases were diluted with nitrogen a portion of this gas was fixed as cyanide. An elaborate series of experiments between 720° and 1120° was conducted by Voerkelius,[4] who found that the yield of hydrogen cyanide was favored by the higher temperatures, faster rates of flow, and dilution of the gas mixture with illuminating gas. The character of the catalyst had a large influence on the decomposition of the ammonia and hydrogen cyanide, porous materials being very effective. All of these investigations were, however, of the nature of rate measurements rather than of equilibrium experiments.

The reaction involved in the work just mentioned seems well suited in many ways for a study of the stability of hydrogen cyanide at moderately elevated temperatures. The equilibrium constant becomes measurable at about 500°, and a combination of this with the reliable work of Haber and his associates on the dissociation of ammonia enables one to calculate directly the equilibrium between hydrogen cyanide and its elements, and hence its free energy of formation. It is true that at temperatures where the constant begins to become measurable ammonia is nearly completely dissociated so that the ultimate equilibrium mixture would contain very little ammonia and a mere trace of hydrogen cyanide with a great excess of hydrogen and nitrogen. The problem of this work was, therefore, to find conditions under which the ammonia dissociation is slow but the desired equilibrium is rapidly established, so that it can be studied as a metastable state.

The investigation was suggested by Professor A. A. Noyes, to whom the author is indebted for much valuable advice. The work was assisted by a grant made to Professor Noyes by the Carnegie Institution of Washington.

## Apparatus and General Procedure

**The Apparatus.**—The schematic diagram of the figure shows how the experiments were conducted. A constant-flow method was used, a mixture of gases being passed continuously over a heated layer of charcoal contained in a silica tube, and the resulting mixture being absorbed or collected for analysis. The gaseous mixture was diluted with nitrogen, this being found more convenient than to work under reduced pressure.

The left side of the diagram represents the arrangement for mixing the gases to be passed into the reaction tube. The ammonia was supplied from a cylinder, and the

---

[3] Lance, *Compt. rend.*, **124**, 819 (1897).

[4] Voerkelius, *Dissertation*, Hanover (1909); *Chem.-Ztg.*, **33**, 1078, 1090 (1909); see *C. A.*, **4**, 1653 (1910).

nitrogen was prepared by removing oxygen from the air. Into the nitrogen could be introduced any desired proportion of hydrogen cyanide by the use of the saturator S, which contained an acid solution of sodium cyanide of suitable concentration; a by-pass allowed the supply of hydrogen cyanide to be cut off when desired. Capillary flow meters M were provided for convenience in controlling the gas mixtures.

The charcoal was confined between two graphite plugs in the center of a long silica tube within the furnace F. A thermocouple junction was imbedded in the charcoal, the junction and leads L being contained in a small porcelain tube for protection. The reaction mixture of gases was rapidly withdrawn from the catalyst through a Pyrex capillary C, and passed to the absorption and collection apparatus.

The ammonia and hydrogen cyanide were absorbed in distilled water by the use of two spiral absorption bottles, only one of which, A, is shown in the diagram. The gas-washing spiral, as indicated in the sketch, was so constructed as to have a very small dead gas space, and as it was removable the titrations could be carried on in the absorption bottles. In Runs 1–4 a small U-tube containing pure soda lime slightly moistened was located between the reaction chamber and the absorption bottles and served to collect all the cyanide.

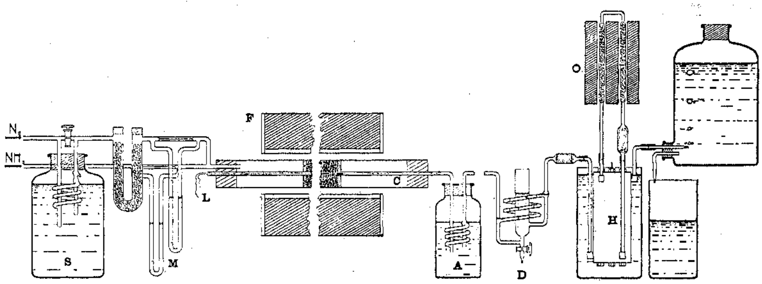

Fig. 1.

The gas from the second absorber was dried by passing it through a spiral sulfuric acid washer D and a phosphorus pentoxide tube. It then flowed through a device H, for determining the hydrogen content by thermal conductivity. This method, developed at the Bureau of Standards,[5] seemed especially suitable, as the gas mixture at this point contained only nitrogen and hydrogen, and its thermal conductivity could be readily compared with that of the gas after the hydrogen had been removed by heated copper oxide (contained in the furnace O of the diagram). The volume of nitrogen remaining was determined by weighing the water it displaced.

**The Charcoal.**—In Runs 1–4 inclusive a very active charcoal supplied by the Fixed Nitrogen Research Laboratory was used. This was found to be very effective in establishing the desired equilibrium, and yet did not decompose the ammonia at a rapid rate. This was to be expected, since charcoal is not a good catalyst for the ammonia synthesis. In Runs 5 and 6 the charcoal was further purified by heating it in a stream of chlorine at 800° for some hours, and then washing it in a stream of nitrogen under reduced pressure. The activity of the carbon was somewhat decreased by this process. In all cases the carbon was evacuated, and washed with a stream of nitrogen at about 500° before using, and the reaction mixture was passed over it for about half an hour before the issuing gases were collected. In Runs 1–4 the charcoal layer was 18 cm. long and 2.8 cm. in diameter; in Runs 5 and 6, it was 6.5 cm. long and 2.5 cm. in diameter.

---

[5] Weaver, Palmer, Frantz, Ledig, Pickering, *J. Ind. Eng. Chem.*, **12,** 359 (1920).

## Analytical Methods

**Analysis of Ammonia.**—The ammonia was titrated in the absorption vessels with sulfuric acid.

**Analysis of Cyanide.**—Very small amounts of cyanide had to be determined, since it was necessary to work at temperatures where the equilibrium is far in the direction of ammonia. In Runs 1–4, where the cyanide was absorbed on soda lime, a procedure similar to that recommended by Lavialle and Varenne was used.[6] The soda lime containing the cyanide was transferred to a casserole and moistened with a solution of sodium polysulfide. The mixture was evaporated to dryness and the resulting thiocyanate was dissolved in a little dil. sulfuric acid solution and a slight excess of calcium carbonate was then added. After filtering and evaporating the solution to dryness the residue obtained was dissolved in a little dil. sulfuric acid and titrated with 0.005 $N$ silver sulfate solution, using ferric sulfate as an indicator. As the end-point was found to be greatly influenced by various conditions, it seems possible that these determinations may be considerably in error, but not more than by 15%. In the last two experiments the hydrogen cyanide and ammonia were absorbed in the same vessel; and, after the ammonia was titrated, sodium bicarbonate was added and the cyanide was titrated with 0.003 $N$ iodine solution, with starch as an indicator. This method was calibrated under the conditions prevailing in the experiments and gave consistent results. Probably the separate determinations were not in error by more than 5%.

## Preliminary Experiments

Before attempting a study of the equilibrium the possibility of side reactions was investigated under the conditions to be used. Of these the two most probable ones are the formation of methane and of amines. By the reduction of hydrogen cyanide at 110° in the presence of platinum black, methyl amine is produced.[7] With nickel as a catalyst at 250°, ammonia, methyl, dimethyl and trimethyl amines are produced.[8]

Experiments failed to show the formation of a detectable amount of methane at 500° when hydrogen was passed over the charcoal. A gas containing about 30% of hydrogen cyanide and 70% of hydrogen was then passed over the charcoal under the conditions later employed in the equilibrium experiments. When the gas issuing from the charcoal was passed through water, the resulting solution gave a strong test for ammonia with Nessler's reagent, while a portion acidified with hydrochloric acid and evaporated to dryness failed to give the test for amines with chloranil.[9]

---

[6] Lavialle and Varenne, *J. pharm. chim.*, **17**, 97 (1918); see *C. A.*, **12**, 1159 (1918).

[7] Debus, *Ann.*, **128**, 201 (1863).

[8] Sabatier and Senderens, *Compt. rend.*, **140**, 483 (1905).

[9] Tsalpatani, *Chem. Zentr.*, **79**, 299 (1908).

This test was found to give a very distinct result with as small a quantity as 7 mg. of dimethylamine hydrochloride.

### The Equilibrium Experiments

The accompanying table gives the results of six equilibrium experiments. In half of these the gas introduced into the reaction tube was a mixture of ammonia and nitrogen. In the other cases the equilibrium was approached from the hydrogen cyanide side by adding this gas to the ammonia mixture in from three to four times the concentration found after equilibrium was attained. Hydrogen was not added, as this was supplied by the decomposition of the ammonia. It was not feasible to approach equilibrium starting with mixtures of pure hydrogen cyanide and hydrogen, either because of poisoning of the catalyst or of some peculiarity in the rate of reaction when the concentration of the former gas was large.

After bringing the charcoal to temperature in a stream of nitrogen, the ammonia mixture was passed over it for 30 minutes or more before the reaction gases were collected for analysis. The rate of flow and the temperature were kept practically constant during each run.

The first row of the table indicates the total duration of a run, the second the temperature on the absolute scale, and Rows 3–6 give the analysis of the total reaction mixture collected during a run. In Row 7 is given the total pressure in the reaction chamber, and in Row 8 the equilibrium constant $K$, at the average temperature of the experiment, calculated by the equation: $K = p_{H_2}p_{HCN}/p_{NH_3}$. In the final row the constants have been corrected to 800° A. in the way described below.

THE RESULTS OF THE EQUILIBRIUM MEASUREMENTS

| Run no | 1 | 2 | 3[a] | 4[a] | 5[a] | 6 |
|---|---|---|---|---|---|---|
| Time, mins. | 112 | 90 | 120 | 130 | 160 | 240 |
| Abs. temp | 801 | 811 | 807 | 793 | 785 | 803 |
| Millimoles $H_2$ | 0.535 | 0.756 | 0.439 | 0.686 | 0.084 | 0.103 |
| Millimoles HCN | 0.0205 | 0.0462 | 0.079 | 0.055 | 0.065 | 0.073 |
| Millimoles $NH_3$ | 27.3 | 44.4 | 38.1 | 54.3 | 25.8 | 29.8 |
| Millimoles $N_2$ | 23.4 | 59.6 | 64.6 | 85.8 | 32.3 | 38.3 |
| Total pressure (mm.) | 747 | 744 | 745 | 745 | 747 | 747 |
| $K \times 10^6$ | 7.7 | 7.3 | 8.6 | 4.9 | 3.5 | 3.7 |
| $K_{800°} \times 10^6$ | 7.4 | 5.0 | 6.7 | 6.2 | 5.9 | 3.3 |

[a] In these experiments equilibrium was approached from the ammonia side.

A few experiments at higher temperatures indicated that the equilibrium changed as was to be expected from the approximately known heat of reaction, but at these temperatures the results were too erratic to lead to a more accurate determination of this heat change.

Some experiments were undertaken to determine the relative rates at which the equilibrium was established and at which ammonia and hydrogen cyanide decomposed. The difficulties of exact analysis made it impossible to separate the effects of the concurrent reactions. It was found that the rate at which hydrogen cyanide combines with hydrogen does not increase with the first power of the hydrogen cyanide partial pressure, but even when nitrogen containing considerable cyanide was passed over the catalyst, the rate at which hydrogen united with the cyanide was high in comparison with the rate at which it was produced by the decomposition of the cyanide. The most conclusive reason, however, for believing that an equilibrium was really obtained is that the "constants" are not affected by the direction of the approach to equilibrium.

## The Free Energy of Hydrogen Cyanide

The available heat data relating to hydrogen cyanide are meager and probably not very accurate. For the molal heat of combustion of this gas at 18°, Thomsen gives 158,600 calories and Berthelot[10] 159,300 calories. These values are in fair agreement and are probably more accurate than the result obtained by more indirect methods. The mean value 158,900 calories, combined with the heat of combustion of graphite (94,250 cal.)[11] and the heat of formation of water (68,330 cal.)[12] gives 30,500 calories for the heat content of 1 HCN at 18°.

Heat-capacity data are lacking, but it seems reasonable to assume that hydrogen cyanide has nearly the same values as carbon dioxide. Like this gas it apparently exhibits the absorption spectrum of a diatomic gas in the infra-red, but like this gas it probably also picks up energy more rapidly at elevated temperatures than the diatomic gases. The molal heat capacities assumed for hydrogen, nitrogen and graphite are those given by Lewis and Randall.

A combination of these data yields for the heat content of hydrogen cyanide this formula: $H = 30{,}600 - 0.60T + 0.00068T^2 - 0.00000022T^3$. This gives for the heat content at 800° A. the value 30,400 cal. Haber[13] in his summary of the measurements on the ammonia equilibrium gives for the heat content of ammonia a formula which leads to the value —13,000 calories at 800° A. Combining these data we obtain the value 43,400 cal. for the increase in heat content attending the reaction $NH_3 + C(s) = HCN + H_2$. Assuming this value to be practically constant over a small temperature range, it was used in the van't Hoff equation to correct the values of the equilibrium constant of this reaction to 800° A. In this way the constants given in the last row of the table were obtained. The mean value of these constants is $5.8 \times 10^{-6}$. The corresponding free-energy increase attending the reaction is 19,200 cal. Haber gives a form-

[10] Berthelot, *Ann. chim. phys.*, [5] **23**, 252 (1881).

[11] Roth and Wallach, *Ber.*. **46**, 896 (1913).

[12] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, **1923**, p. 477.

[13] Haber, *Z. Elektrochem.*, **20**, 597 (1914).

ula for the calculation of the ammonia equilibrium constant over a range of temperatures. Probably the value for the free energy of ammonia at 800° A., 9220 cal. as calculated by its use, is not greatly in error.

These data lead to the value 28,400 cal. for the free energy of hydrogen cyanide gas at 800° A. Combining this with the heat data mentioned we obtain for the free energy of this gas as a function of temperature: $F = 30{,}600 + 0.60T\ ln\ T - 0.00068T^2 + 0.00000011T^3 - 6.3T$. This leads to the special value 29,700 cal. at 298° A. Lewis and Randall give the fairly concordant value 28,910 cal., but this was obtained very indirectly through the combination of results on a series of equilibria.

## Summary

A study of the equilibrium of the reaction between ammonia and carbon, yielding as products hydrogen cyanide and hydrogen, has been described; and the free-energy decrease attending the reaction at 800° A. has been calculated. By the use of data on the ammonia dissociation and of heat data, the free energy of hydrogen cyanide gas has been expressed as a function of temperature, and the special values at 800° and 298° A. have been given.

PASADENA, CALIFORNIA

---

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

# HYPONITRITES[1]

BY LAUDER W. JONES AND ALFRED W. SCOTT

RECEIVED MAY 31, 1924 PUBLISHED OCTOBER 4, 1924

Experiments which required silver hyponitrite in considerable quantities compelled us to seek a satisfactory method for its preparation.

The various preparative methods employed in the making of hyponitrites may be classified into two major groups: first, those which employ compounds whose molecules contain one atom of nitrogen; second, those which use substances with two atoms of nitrogen in their molecules.

In the first group, we may place all of the methods based upon the reduction of nitrates, nitrites[2] or nitric oxide and upon the direct[3] or indirect[4] oxidation of hydroxylamine.

The second group of methods shows considerable diversity also. Many of the proposed syntheses depend upon the interaction of nitrous acid and

---

[1] The experiments described in this article were undertaken jointly by the authors at Princeton University. They were completed at the University of Georgia.

[2] (a) Divers and Haga, *J. Chem. Soc.*, **47**, 623 (1885); **75**, 87, 95 (1899). (b) Hantzsch and Kaufmann, *Ann.*, **292**, 317 (1896). (c) Raschig, *Ann.*, **241**, 230 (1887). (d) Divers and Haga, *J. Chem. Soc.*, **55**, 765 (1889). (e) Kirshner, *Z. anorg. Chem.*, **16**, 424 (1898).

[3] Ref. 2 b. Thum, *Wien. Monatsh.*, **14**, 294 (1893).

[4] Piloty, *Ber.*, **29**, 1559, 2324 (1896). Angeli, *Gazz. chim. ital.*, **26**, 17 (1896); **30**, 593 (1900). Angeli and Angelico, *ibid.*, **31**, 15 (1901); **33**, 245 (1903).